MICROPOROUS CARBONS AS ADSORBENTS FOR METHANE STORAGE

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ABSTRACT

The volume available for gas storage is often limited. Because the density of the adsorbate is greater than the gas phase above it, gains in storage capacity at moderate pressures can be achieved through the use of adsorbents. Adsorbent storage systems can be used for various gases such as natural gas, hydrogen, ammonia or HFC's.

Optimal storage capacity will occur when that fraction of the storage volume that is micropore is maximized with no void or macropore volume. The average micropore diameter should be that most suited to the adsorbate molecule. In practice, this is difficult to achieve.

Carbons with high methane uptake per unit mass but with low bulk density may not be as suitable as carbons with lesser methane uptake but which have higher bulk density. The method of preparation of the adsorbent carbon is therefore very important. Conditions must be such that macropore formation is controlled and micropore enhanced.

INTRODUCTION

The acceptance of natural gas as a vehicular fuel has been slow, mainly due to a limited driving range. This range is restricted because of a much lower fuel or energy density than gasoline in the available storage volume. Initially an upper pressure of 2400 psi (16.3 MPa), equivalent to about 180 volumes of gas at STP per unit volume of storage, was used. This has been increased to 3000 psi (20 MPa), and even higher pressures have been called for.

The storage capacity of natural gas (methane) can be increased over that of compression alone through the use of an adsorbent. Methane density in a storage vessel at 3.4 MPa (500 psi) can be increased by a factor of four or more over that of compressed gas by using adsorbents, (1)(2). Thus through the use of carbons, methane storage densities of 180 V/V, equal to that of CNG at 2400 psi can be achieved at only one quarter or one fifth of the pressure, making adsorbed natural gas (ANG) an alternative to CNG. It should be noted here that storage is considered taking place at ambient temperature and cooling is not considered practical.

This increase in methane storage density in the storage vessel over CNG is due to adsorption of methane molecules in the micropore of the carbon. Therefore a carbon with a large micropore volume will adsorb more than one with a lesser micropore volume. However, these micropore volumes must be related to the storage vessel volume and not simply to a unit mass of carbon. The bulk or packing density of the carbon adsorbent therefore becomes very important.

When a vessel is packed with carbon, the volume occupied by the carbon atomic matrix is not available to methane. The fraction of the vessel volume which is void space or macropore volume will only store methane as compressed gas and that fraction which is micropore is the only one where there will be an increase in methane density. It follows, therefore, that a vessel packed without void space with a totally microporous carbon, maximized for microporosity, would be ideal.

Some carbons are closer to this ideal than others. The objective of this paper is to examine the characteristic properties of several carbons and relate these to methane storage. In doing this, it should be possible to consider different approaches to the preparation of adsorbent carbons in order to optimize them for methane storage.

Recent theoretical studies by Gubbins (3) and Myers (4) have shown that an optimal micropore would have a wall separation of about three to four methane diameters. The conclusion by Myers was that a highly idealized carbon composed of single graphitic layers 0.114 nm apart would store 209 V/V at 3.4 MPa.

Brookhaven National Laboratory have measured deliveries of methane from 3.4 MPa in excess of 150 V/V from carbon filled vessels at ambient temperature suggesting that storages of about 180 V/V have been achieved (5). Chaffee has prepared a carbon from Australian lignite which stored 202 V/V at 4.0 MPa (6).

EXPERIMENTAL
BET surface areas (7) and Dubinin-Radushkevich (8) micropore volumes for all the carbons were obtained using the Micromeretics ASAP 2000 to measure the nitrogen isotherm at 77K.

Mercury porosimetry measurements were carried out using the Quantachrome Autoscan 60 to obtain macropore volumes, and densities (9).

Methane isotherms were measured at 298K with the Sartorius M-25 high pressure balance. Buoyancy corrections were made by using equal weights of aluminum and magnesium as the counterweight. The deviation from ideality by methane was corrected using the data of Douslin et al. (10). For single stage compression, the practical benchmark pressure of 3.4 MPa (500 psi) was used in the comparison of the performance of each carbon.

TABLE 1

Carbons		BET Surface Area m²/g	D-R Micropore Volume mL/g	Packing Density g/mL	Hg 1 atmos Particle Density g/mL	Mercury 60K psi Density g/mL	Macropore Volume mL/g	Methane Uptake 298K 500psia mgs/g
Norit	EX6	445	0.23	0.71	1.15	1.40	0.16	48
Calgon	SGL	900	0.4	0.49	0.78	1.33	0.53	65
Calgon	BPL	1030	0.47	0.44	0.75	1.11	0.43	75
Darco	Vapure 184-01	1095	0.51	0.58	0.81	1.19	0.39	84
ACCarbone	CNS 196	1190	0.49	0.44	0.85	1.22	0.36	80
Norit	R3	1270	0.58	0.42	0.65	1.06	0.80	92
Kureha	BAC	1350	0.60	0.59	0.90	1.08	0.19	99
California	GMS-70	1502	0.64	0.41	0.68	1.11	0.57	108
Barnebey	MI	1730	0.71	0.46	0.71	1.05	0.46	109
Sutcliffe	GS/60	1860	0.82	0.34	0.60	0.91	0.57	129
Osaka	M-30	2415	1.11	0.34	0.35	0.88	1.72	144
Kansai	Maxsorb	2671	1.29	0.27	0.29	0.90	2.34	164
Electrosynthesis EL		2798	1.58	0.24	0.30	0.92	2.25	170

Table 1 lists the commercial carbons studied. These carbons come from a variety of precursors and have been made using different preparative methods. They cover a range of surface area and are listed on this basis. The Dubinin-Radushkevich micropore volume relates in a linear manner to the surface area. Methane uptakes at 3.4 MPa (500 psi) have been taken from the 298K isotherms, some of which are shown in Figure 1.

Figure 1

Methane Isotherms at 298K

BPL   BAC   MI   GS/60   Maxsorb
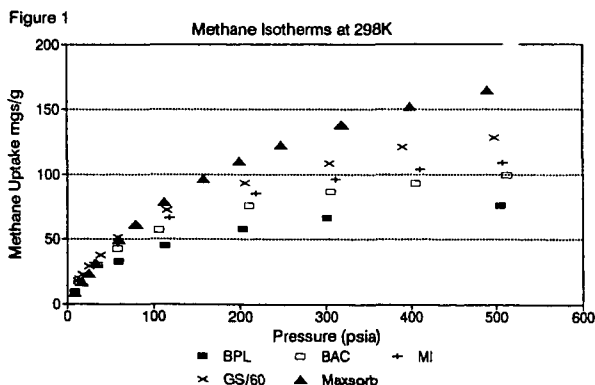
DISCUSSION

Many workers do not have the equipment to measure high pressure isotherms, but nearly every laboratory is able to measure surface areas and micropore volumes. Figure 2 shows the relationship between the 77K nitrogen surface area and the methane uptake at 3.4 MPa and 298K for these carbons. A more recent method, the alpha-s method, (11), distinguishes between micropore and surface area due to mesopore. This may be a better way of relating the extremely high surface area carbons to methane adsorption but has not been used in this paper. This relationship in Figure 2 is based on mass of adsorbent. The problem of gas storage is one of limited volume, and so the amount of methane which is stored in a vessel will be the product of the mass adsorption and the packed density of the carbon, plus methane stored as gas phase in the void and macropore volume.
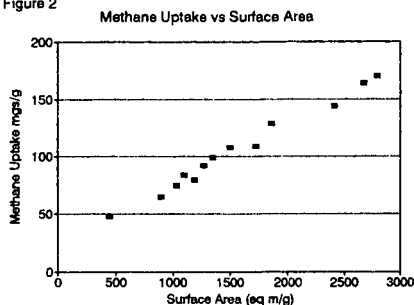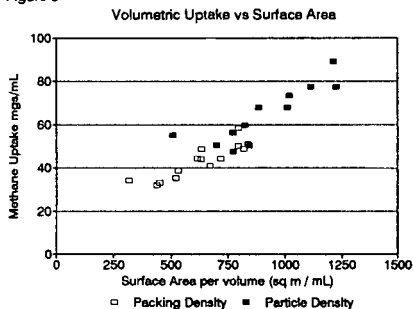
Figure 2

Methane Uptake vs Surface Area

Figure 3

Volumetric Uptake vs Surface Area

Because high surface area carbons often have low packing densities, they are often superseded in the amount of methane adsorbed per unit volume by carbons with greater packing densities. Figure 3 shows the surface area per mL with the methane adsorbed per mL of vessel using the normal packing density, (open squares). Additionally, Figure 3 illustrates the increase in adsorbed methane in the storage vessel if it could be packed to the particle density of the carbon. This latter situation is unrealistic but does serve to show the great gains to be made if packing density can be increased and voids reduced. The carbon which is most suited for methane storage is the Kureha BAC carbon, one of modest surface area per gram but which has both a high packing and particle density and low macropore volume. Figure 4 clearly shows that the high surface area per gram carbons are less suited for methane storage. Their large macropore volumes are mainly responsible for this.

Since storage of methane is taking place some hundred degrees above its critical temperature, adsorption will occur principally in the micropore. The methane density at 3.4 MPa and 298K in the micropore can be estimated. This has been plotted against the micropore volume per gram of carbon in Figure 5. Those carbons with large micropore volume (and high surface area) have low methane densities suggesting that the pore dimensions may be too large for efficient methane storage at temperatures well above its critical temperature.

Figure 4

Volumetric Uptake vs Surface Area
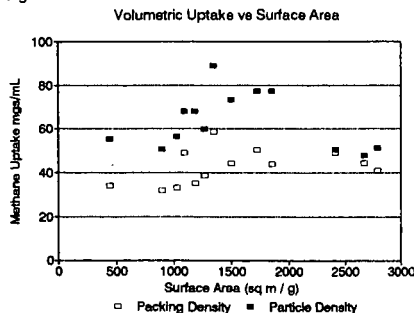
Dignum (12) has shown that the theoretical maximum density for methane at 298K is about 270 mgs/mL of pore. The low surface area Norit EX6 has a high methane density approaching this theoretical value. Takeda MSC-5A (13), a low surface area carbon, 445 m^2/g, has a methane

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density in excess of 200 mgs/mL at 3.4 MPa and 298K. We have also found that unactivated coconut shell and peach pit chars of similar surface area to the Takeda carbon also have similar methane densities. This has also been shown for 5A and 13X molecular sieves (14).

Unfortunately all these materials have low micropore volumes per unit mass or volume and so are unattractive as candidates for methane storage. One carbon, made by the slow pyrolysis of PVDC polymer, has a methane micropore density of 219 mgs/mL at 3.4 MPa and 298K (15), suggesting that the pore dimensions are close to ideal. Additionally, about fifty percent of its particle volume is micropore with little or no macropore. It stores in excess of 150 V/V at 3.4 MPa and 298K.

Figure 5

Methane Density vs Micropore Volume
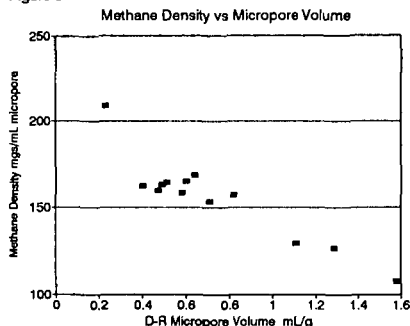
Traditionally carbons have been "activated" by heating them with air, steam or carbon dioxide at elevated temperatures. This results in carbons with higher surface areas per unit mass of carbon but with reduced packing and particle density. The reduction in density, however, is due not only to the creation of micropore but also to macropore formation. This macropore does not contribute to improved methane storage. The three high surface area carbons in Table 1 all have macropore volumes in excess of fifty percent of their particle volume.

The above shows that carbons can be made which have suitable micropore dimensions for methane storage, the problem is that these are not present in sufficient quantities to provide storage in excess of 180 V/V at 3.4 MPa and 298K. Methods of preparation which enhance micropore formation or reduce the production of macropore are desirable for gas storage carbons.

Figure 6

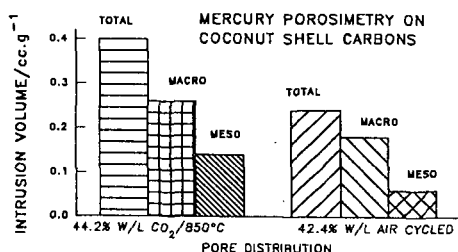MERCURY POROSIMETRY ON COCONUT SHELL CARBONS

PORE DISTRIBUTION

Figure 6 shows the meso and macropore volume for two CNS carbons. Both have been activated to about the same weight loss or burn off. One has been reacted with carbon dioxide at 850°C, a more conventional activation method. The other has been produced by cycling at low temperature with air followed by higher heat treatment under nitrogen (16). The latter method gave a carbon which had reduced macropore and mesopore volume, illustrated in Figure 6. It also had increased particle and packing density and showed an 18% increase in methane storage over the more conventionally prepared carbon.

Although storage has been emphasized in this paper, delivery from the storage vessel is perhaps more important. Delivery is considered as the amount of gas which is obtained from the vessel when the pressure is reduced to atmospheric. Carbons which have very narrow pore dimensions show high methane densities in these pores. They also have very steep Type 1 isotherms (17) and retain large amounts of methane at atmospheric pressure. PVDC carbon is a typical example of this type of carbon and retains at one atmosphere about thirty percent of the methane stored at 3.4 MPa. Treatment of this carbon with the air cycling technique improves the methane delivery.

Figure 7 relates carbon packing density and methane adsorption at 3.4 Mpa and 298K to delivery. The two curves for 100 and 150 V/V have been generated taking into account both the methane

desorbed isothermally and additionally the methane which would be stored as gas phase in void and macropore volume. The carbons from Table 1 are plotted using the normal packing density (open squares). They fall considerably short of the desirable 150 V/V delivered, however, if they were packed to their particle density (closed squares) then they come much closer to the goal.

Figure 7

Density / Adsorption
For 100 - 150 V/V Delivery

■ Particle Density   □ Packing Density
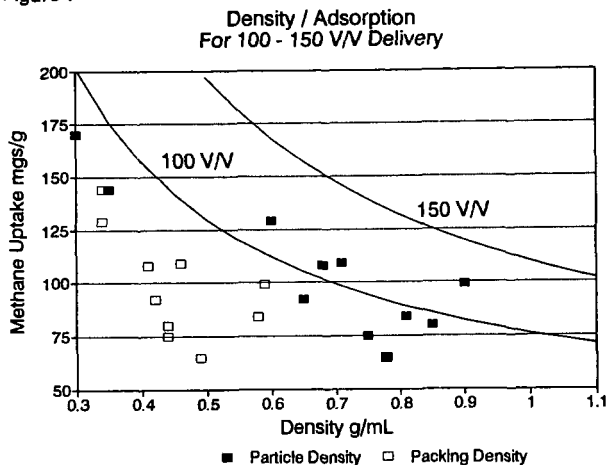
CONCLUSION
High surface area, low density carbons with high methane uptake per unit mass store and deliver less methane than some carbons with lower surface area but higher density. Carbons which have been optimized for micropore volume per unit volume will be most suited for ANG or other gas storage.

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